HIGH EFFICIENCY, STRUCTURED-PACKING CATALYSTS WITH ACTIVATED CARBON FOR SO$_2$ OXIDATION FROM FLUE GAS

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ABSTRACT
Monolithic or Sulzer CY gauze structured packings were loaded with hydrophobized activated carbon. Studies of their activity for SO$_2$ conversion to sulfuric acid were carried out with respect to principal scale-up variables of the process: temperature, pressure drop, periodic vs. continuous operation, gas and liquid flow rates. High conversions, high catalyst efficiency, and low pressure drops, long catalyst lifetime, easy of handling catalyst packings are some of the outstanding features of the system.

INTRODUCTION
Environmental regulations impose a removal of at least 85 - 90% of sulfur from fuel. Huge volumes of flue gases (e.g., that of a 700 MW oil-fired power station is equivalent to ca. 2 million cubic meters per hour) containing up to 0.3% SO$_2$, impose severe requirements on industrial flue gas clean-up plants: low pressure drops at high gas flow rates (>10,000 h^{-1}), sulfuric acid solutions of at least 15 wt% concentration, small volume, easy-to-handle catalysts, long catalyst lifetimes, no waste products generated by the exhausted catalyst, almost constant temperature profiles.

One of the most attractive method is to use activated carbon catalyst to oxidize SO$_2$. Over the last three decades, numerous studies have described the oxidation of SO$_2$ on activated carbon catalysts either in gas-solid system when H$_2$SO$_4$ is thermally desorbed, or in gas-liquid-solid systems (trickle-bed or slurry) when H$_2$SO$_4$ is washed with water [1-10]. As the gas-solid system involves catalyst reheating to accomplish desorption in which the adsorbed sulfuric acid reacts with carbon to form CO$_2$, H$_2$O and SO$_2$, the three phase system seems to be more attractive. Use of large-scale trickle-bed reactors is still hindered by some specific drawbacks: very low effectiveness factor (0.021 for 2.59 mm particle diameter, and 0.45 for 99 μm) , high pressure drops over the catalyst bed, maldistribution of various kinds (including a non-uniform access of reactants to the catalytic surface), rapid SO$_2$ breakthrough due to sulfuric acid entrapped in pores, and very low concentrations of the sulfuric acid in the effluent. Recognizing that reaction in dumped catalysts is controlled by mass transfer to and from the catalyst, we have studied a three-phase reactor in which the catalyst is deposited as a thin layer (micrometers) on screens of appropriate hydrophobicity. Either monolithic or static mixers configurations, known for their low pressure drops, are used. Their hydrophobic-hydrophilic characteristics determine the distribution of dry and wet zones that spontaneously change with time ensuring both higher access for gaseous reactants to the catalyst and more efficient removal of product from it. The frequency of shifting depends on the gas and liquid flow rates and the catalyst geometry which determines the flow pattern. Because of this dynamic alternation, almost the entire catalytic surface is involved in the oxidation process.

SO$_2$ oxidation on activated carbon involves a reaction among three species: SO$_2$, O$_2$, and H$_2$O adsorbed on the carbon surface. A reaction of three adsorbed species simultaneously is, statistically speaking, possible but quite unlikely. Nevertheless, activated carbon has an affinity for molecular SO$_2$, 2.7 times larger than for oxygen [13]. As the solubility of SO$_2$ in water is more than 10 times larger than for oxygen, O$_2$ is the thus limiting reactant despite a 100 fold larger partial pressure than that of sulfur dioxide. It is thus intuitive that carbon surfaces are readily populated with SO$_2$, so that the rate of uptake of oxygen on the active sites is almost certain to be rate-limiting. Infrared analysis demonstrated that in the presence of water vapor and oxygen, sulfuric acid is formed on

carbon. In addition to sulfuric acid, a small quantity of chemisorbed SO_2 was found, as well as some residual water [11]. Once H_2SO_4 is formed, it becomes a competitor for active sites, along with SO_2, O_2, and H_2O. Meanwhile, sulfuric acid decreases SO_2 and O_2 solubilities but not in the intrinsic rate of surface reaction itself, within reasonable limits (up to 30 wt% H_2SO_4).

Sulfuric acid formation is ensured by the water vapor present in flue gas, liquid water only playing the role of product carrier from the catalyst pores. Therefore water flow rate affects the liquid film resistance to the reactants transferring from gas onto the active catalyst sites. The preparation method of our catalysts ensures a hydrophobic catalytic surface still keeping a polar character inside the pores. As was shown [16], pyrone and pyrone-like structures are responsible for the catalytic activity. The presence of hydroxyl groups on the activated carbon provides an additional opportunity for controlling the hydrophobicity inside the pores in order to obtain a controlled wet-proofing.

EXPERIMENTAL
Catalyst
Two basic types of structured packings were used: monoliths and static mixers (Sulzer CY) gauze. Monoliths were built up by rolling together a corrugated gauze, on which activated carbon was loaded using a hydrophobic binder, with a flat screen which was either hydrophilic or hydrophobic. Monolithic catalysts were supplied by Atomic Energy of Canada Limited (AECL). Static mixers were supplied by Sulzer Chemtech, Winterthur, Switzerland, and loaded with activated carbon by AECL. Properties of activated carbon and catalyst beds are given in Table 1. Centaur^{TM} activated carbon (Calgon Carbon Corp.) with an average particle diameter of 0.3 μm has been used for loading the screens in all runs. BET surface areas of the bound carbon were determined at -195.5^{o}C by nitrogen adsorption using a Quantachrome Autosorb Automated Gas Sorption System, Micropore Version 2.44. Typical values were 139.9 m^2/g for overall surface area, 95.7 m^2/g for mesopore area, and 44.2 m^2/g for micropore area.

Table 1. Properties of activated carbon and catalyst beds.

Catalyst	Type	Carbon type/weight (g)	Height cm	Cross-section area cm^2	Volume cm^3
QA 95-8	Monolith-hydrophilic sep. screen, 120 mesh	Centaur/ 10.23	3x10	19.63	589.1
QA 95-9-0	Monolith-hydrophilic sep. screen, 20 mesh	Centaur/ 23.43	3x10	19.63	589.1
QA 95- 9-1	Monolith-hydrophilic sep. screen, 20 mesh	Centaur/ 22.52	3x10	19.63	589.1
QA 95-11-0	Monolith-hydrophilic sep. screen, 28 mesh	Centaur/ 28.44	1x10	19.63	196.3
QA 95-11-1	Monolith-hydrophobic sep. screen, 28 mesh	Centaur/ 28.44	1x10	19.63	196.3
QA 95-12	Static mixers CY	Centaur/ 23.28	2x15	15.90	476.8

Apparatus
The SO_2 oxidation was carried out in a glass reactor of 600 mm length and 50 mm id. Gaseous reactants and water were fed concurrently in the top of reactor. Water was supplied by a micropump Gear Pump - Model 130/150, (Micropump Corporation, Vancouver, WA), after preheating (as needed) and saturation with oxygen in a saturation column filled with static mixers Sulzer Mellapak 125.Y of polypropylene. An adjustable height spray nozzle was used to distribute washing liquids evenly over the cross section of the reactor. Periodic liquid interruptions were achieved by means of a solenoid valve in the feed line to the reactor vessel. The valve was controlled by a microcomputer through a D/A interface. Feed gas with a volumetric composition of 10% CO_2, 5% O_2, and 0.3 % SO_2 was preheated (as needed) and saturated with water at 45°C correspondent to 10% H_2O in the gas mixture, the balance being N_2. Flow rates of the individual gaseous streams were controlled by mass flowmeters Unit (Unit Instruments, Inc., Orange, CA). The reactor was heated using three heating tapes, and temperatures were measured by 0.2 mm o.d. type K thermocouples and recorded by the data acquisition system. Pressure drop in the catalytic bed was measured with a water-filled manometer connected to taps located above and below the bed. The reactor effluent

was cooled and liquid and gas phases were separated. SO_2 concentration in the gaseous effluent was continuously monitored by a UV spectrometer (Western Research, model 721 AT) and recorded by the data acquisition system. The liquid phase was analysed for H_2SO_4 by titration with 0.1 N solution of NaOH. Sulfur dioxide dissolved in liquid effluent was determined by means of a conventional iodine titration. Typical operation conditions are summarized in Table 2.

Table 2. Operating conditions for the reaction studies.

Temperature, ^oC	23 to 80
Pressure, MPa	1.013 E - 01
Liquid phase	Deionized water (DI), DI + Tween 20 (4 E - 07 mol/l), DI + acetone (20 wt %)
Gas flow rate, m^3/s, at 25^oC	(5.5 to 33) E - 05
Liquid flow rate, m^3/s	(5.3 to 55) E - 09

RESULTS AND DISCUSSIONS

The exploratory investigations were carried out on three main catalytic configurations: monoliths with hydrophilic separation screens (QA 95-9 and QA 95-11-0), monoliths with hydrophobized catalyst and separation screen (QA 95-11-1), and hydrophobized static mixers CY (QA 95-12).
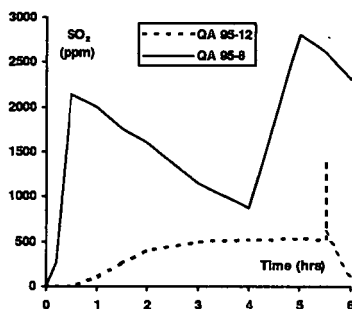

Figure 1. Concentration Profiles of Free SO $_2$ in the Reactor Effluent for Different catalysts

Monoliths with hydrophilic-hydrophobic screens (QA 95-9 and QA 95-11-1) give rise to high liquid static hold-up over the catalyst bed (equivalent to 20 wt% of catalytic stack weight). With these stagnant columns of liquid in each channel, there was poor reproducibility of data preventing a clear conclusion. Obviously, a higher contact time between liquid and catalytic surface improves sulfuric acid removal but, on the other hand, reduces the mass transfer rates of gaseous species onto the catalytic surface. Both periodic operation (flushing periods of 30 to 45 seconds followed by "dry" periods of 255 to 270 seconds) and continuous flushing, gave non-reproducible results. Periods of high conversions alternate with lower removal of SO_2 in a random way due, probably, to a very complex hydrodynamic regime in the channels which creates a "storage effect" of SO_2. A typical concentration profile for the "free" SO_2 released in the effluent is shown in Figure 1 (QA 95-8). In spite of high conversions periods - especially in forced periodic operation - the system didn't permit further studies of the influence of other process variables, because of high oscillations in SO_2 conversions during the same run.

Figure 2. Conversion to H $_2SO_4$ vs. Superficial Liquid Velocity

Initially with low temperature runs, negligible H_2SO_4 is formed in the micropores because of low reaction rate; the diffusing species (SO_2, O_2, and H_2O) fill the micropore volume taking up the available vacant sites. However, beyond this initial period, reaction occurs on a time-scale longer than the adsorption time-scale, the product H_2SO_4 forms and displaces other molecules (SO_2, O_2, H_2O) until a new steady-state between sorption and reaction prevails.
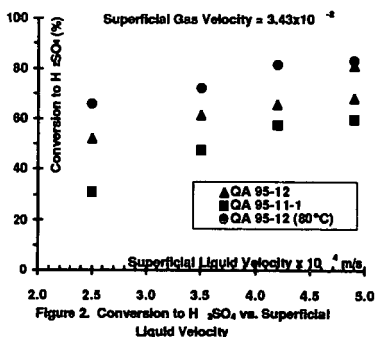
The influence of liquid flow rate on the SO_2 conversion is shown in Figure 2. An increase in conversion is expected due to the improvement of sulfuric acid removal. Obviously, better contact between catalyst surface and washing liquid will facilitate efficient cleaning of the catalyst. Runs with a mixture of deionized water and 20 wt% acetone or with a wetting agent (Tween 20, 10^{-6} M) which facilitate penetration in the meso- and micro-pores and faster removal of sulfuric acid, led to an increase of conversion with 10 to 18%. This is contrary to the contention [8]

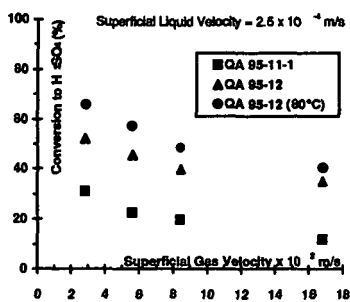that the higher the liquid flow rate the lower is the fraction of SO_2 oxidized to sulfuric acid. In the range of interest, due to the hydrophobicity of the catalyst surface, reactants are mainly supplied directly from the gaseous phase.

Figure 3. Conversion to H $_2SO_4$ vs. Superficial Gas Velocity

Meanwhile, at temperatures higher than 80°C, sulfuric acid present in catalyst pores has such high concentrations as to allow the use of sulfuric acid solutions (7 to 15%) as washing liquids. In this way it is possible to use optimum flow rates of liquid, without an undesirable dilution of the solution. On the other hand, preliminary tests done with an organic substrate (dodecylbenzene) gave very promising results in a reactive removal of sulfuric acid with production of surfactants, which might be a novel route for

SO_2 removal.

Increasing the gas flow rate cause a decrease in conversion (Figure 3). The oxidation rate lagged behind the adsorption step rate [1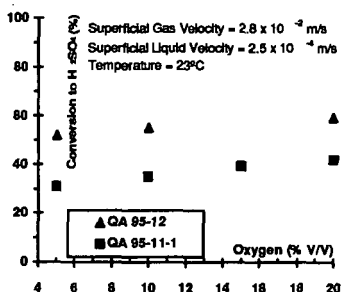6]. As expected, shorter contact time between reactants and catalyst reduced conversions. The most likely reasons for this are correlated with the efficiency of sulfuric acid removal and/or oxygen activation rate. An enhance of catalytic activity has been achieved by doping the internal surface with typical oxidation catalysts, e.g., oxides of cobalt, chromium, and vanadium, or phthalocyanines [14,15].

Figure 4. Conversion to H $_2SO_4$ vs. Oxygen Concentration in the Feedstock

It is important to mention that even at the highest gas and liquid flow rates, the pressure drops over the catalytic bed were less than $25x10^{-2}$ kPa.m^{-1}. The lowest values were achieved with hydrophobic monoliths.

One of the most important requirements in the oxidation process is to supply sufficient amounts of oxygen onto the active sites. The oxygen adsorption onto the catalytic surface follows a Henry type isotherm; hence an increase in its partial pressure will increase the available active oxygen and will provide an increase in conversion. As shown in Figure 4, an increase in the range of 5 to 20 % O_2, led to higher conversion. Further investigations are necessary to develop a better correlation of oxygen concentration with temperature and nature and size of liquid flow rate.

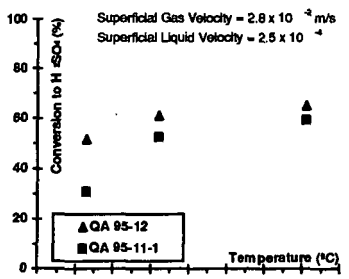Temperature has a complex effect on the oxidation process. An increase in temperature leads to higher reaction rates and higher concentrations of the sulfuric acid loaded in the pores. However, temperature also determines lower solubilities of reactants in the liquid inside and outside the pores with a subsequent decrease of reaction rate. In our situation, experimental data confirm an enhancement of conversion to sulfuric acid with temperature increase. Values as high as 92% were achieved at 80°C. Experiments in the range of 90 to 120°C are now in progress. The hydrophobic character of the catalytic surface and the continuous alternation of dry and wet surfaces permits easier transfer of reactants to the catalyst surface directly from the gaseous phase, making the contribution of dissolved species less important (Figure 5).

Figure 5. Conversion to H $_2SO_4$ vs. Temperature

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CONCLUSIONS

Centaur activated carbon bound in a thin layer on monolithic or static mixer packings has been used with very good results for SO_2 oxidation. Conversions of 92% and productivities relative to a unit weight of carbon were achieved. The high catalytic activity shown by the hydrophobic thin layer catalyst appears to benefit from its hydrophobicity to water and short diffusional paths. Investigations on catalytic system behaviour at higher temperatures (100-120°C), using either sulfuric acid solutions or organic substrates, as washing liquids are now in progress. As a consequence of the system features, the use of periodic flushing is expected to enhance catalyst productivity. Very low pressure drops over the catalyst bed, and production of either concentrated solutions of sulfuric acid or sulfated/sulfonated organic substrates make the process very attractive for commercial plants.

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